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PROVISIONAL APPLICATION FOR PATENT COVER SHEET

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Docket Number		26020		Type a plus sign (+) inside this box ->	+
INVENTOR(S) / APPLICANT(S)					
LAST NAME	FIRST NAME	MIDDLE INITIAL	RESIDENCE (CITY AND EITHER STATE OR FOREIGN COUNTRY)		
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TITLE OF THE INVENTION (280 characters max)					
COPPER CMP SLURRY COMPOSITION					
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STATE	VIRGINIA	ZIP CODE	22202	COUNTRY	USA
ENCLOSED APPLICATION PARTS (check all that apply)					
<input checked="" type="checkbox"/> Specification	Number of Pages	18	<input checked="" type="checkbox"/> Applicant is entitled to Small Entity Status		
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METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT (check one)					
<input type="checkbox"/> A check or money order is enclosed to cover the filing fees					
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The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.



No



Yes, the name of the US Government agency and the Government contract number are: _____

Respectfully submitted,

SIGNATURE

Sol Sheinbein

April 8, 2003

Date

25,457

REGISTRATION NO.
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Additional inventors are being named on separately numbered sheets attached hereto

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Copper CMP Slurry Composition

Inventors:

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1. Introduction

Copper is the metal of choice serving as interconnect material in advanced submicron multilevel technologies, because of its low resistivity and high electromigration resistance. Copper damascene process has been developed for advanced interconnects production (1); in this method the dielectric is patterned, followed by a metal deposition and subsequent planarization. Due to the difficulties in patterning Cu using reactive ion etching [RIE] (2), (since the process by-products are not volatile at the temperatures process), other techniques must be considered. Planarization is an important step in damascene process, while the planarization processes is a chemical-mechanical polishing (CMP). Once a wafer is introduced into slurry, several processes and interactions are taking place simultaneously. These processes and interactions include mechanical removal of oxide layers, fluid flow at the interface, chemical passivation, abrasive-solution and abrasive-abrasive interactions and pad type and degradation. Synergism of all of these interactions will lead to rapid global planarization while in many cases antagonism is reported (3). Surface corrugations on a wafer are removed and global planarizing during the CMP process is achieved by both chemical and mechanical forces. Mechanical removal alone may introduce internal stresses into the thin Cu layer, leading to connectors cracking (4). CMP is possible only if it fulfils the following conditions (5): (i) the planarized metals must undergo a rapid self passivation process in the CMP slurry; (ii) active dissolution takes place only at the upper surface sites, where the passive film is removed by a direct contact with the abrasive; (iii) a rapid repassivation of the activated sites in the slurry must occur. Thus, a major requirement for a CMP process is the passivation of copper in the used slurries.

It is clear that the chemical composition of the slurry is the main criteria in order to accomplish the required CMP conditions. Based on Pourdaix diagram (Figure 1) copper can be passivated only in solutions with pH values above 7 (6). This indicates

that neutral or basic solutions can only be considered. One of the solutions that were suggested for use as CMP slurry is ammonium hydroxide solution (NH_4OH) (7).

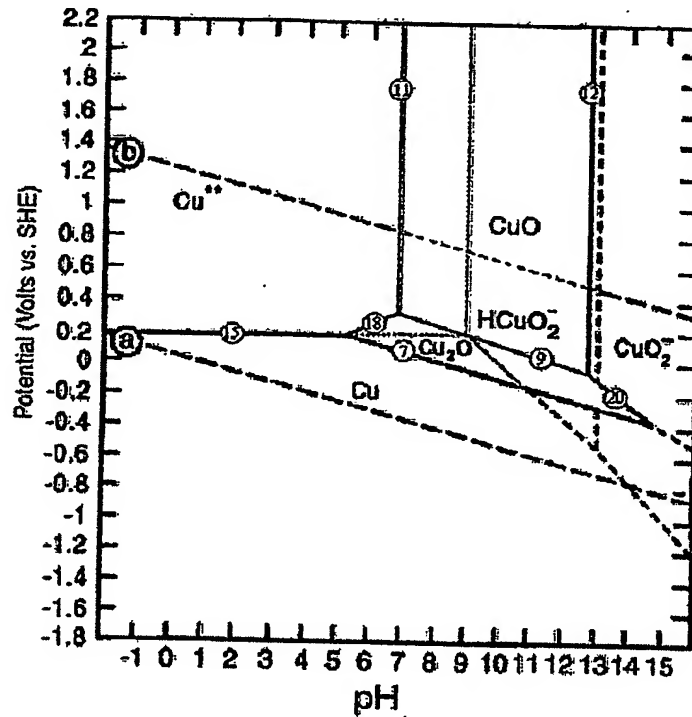


Figure 1. Potential-pH equilibrium diagram of copper-water system at 25°C (considering the solid substances Cu, Cu_2O , and CuO) [$\text{Cu}^{2+}] = 10^{-6} \text{ M}$ ⁴³.

The recommended pH value of NH_4OH solutions in CMP slurry application is ranging between pH 11 and 12 (depending on the solution concentration), since copper passivation can be expected in this pH range (6). However, ammonium hydroxide can provide the conditions for the formation of soluble copper complexes, such as $\text{Cu}(\text{NH}_3)_2^+$ leading to copper dissolution (8). Therefore, the use of ammonium hydroxide based solutions in CMP slurries is not obvious and needs a thorough investigation.

Other most popular solutions suggested as CMP based slurries are acidic solutions, such as nitric acid ($\text{pH} \leq 2$) (9), ferric nitrate ($\text{Fe}(\text{NO}_3)_3$, ($\text{pH} \leq 2$) (10), and peroxide (pH ranging between 3.5 and 4) (11). However, Pourbaix diagram indicates that copper is actively dissolved in solutions below pH 7 (6). It is obvious that acidic solutions cannot provide the conditions for copper passivity and therefore their use in CMP slurries is

problematic. In order to comply with the CMP requirements, the addition of inhibitors [such as benzotriazole, (BTA)] in acidic solutions was suggested (10, 12-15). The addition of BTA results in the formation of a Cu-BTA protective layer, which blocks the copper surface leading to a decrease in dissolution rate of metallic copper. Many authors (10, 12-15) indicated that this protective layer can mimic the behavior of a passive oxide film during CMP process: removal of inhibitor films from upper surface of the copper during CMP would result in an active dissolution of bare sites at the copper surface. Recovering and reformation of a protective film at these sites during further exposure decreases the dissolution rate. It was suggested that repetitive activation and passivation of upper surface sites may result in surface polishing (10, 12-14). However, copper protection with the use of inhibitors is **not effective** in CMP processes, under rapid surface abrading conditions.

2. Experimental

Measurements were conducted in solutions containing ammonium hydroxide, nitric acid and peroxide. All the chemicals were obtained from Aldrich Chemicals and were used without any further purification. Pencil-type copper electrodes were produced by mounting pure copper metal (99.9995 wt.%) rod of 3.5 mm diameter in an epoxy resin. The electrodes were freshly wet-abraded to a 1200 grit finish prior to each experiment. Studying the morphology of the etched copper surface was performed with rounded copper coupons (0.5 cm radius and 2 mm thick, 99.9995% purity). The electrochemical measurements were performed in a three electrode electrochemical cell with the use of potentiostat (273A EG&G). Working electrode potentials are referred to a saturated calomel electrode (SCE) which was connected through a Luggin-Habber capillary tip assembly, while the counter electrode was a Pt-wire. The morphology of the corroded copper samples was studied by scanning electron microscopy (SEM L30 and HRSEM Zeis). Prior to SEM observation the specimens were washed in DI water followed by air drying.

3. Results and Discussion

Previously we reported (16) that copper is actively dissolved in all the commercial CMP solutions. At this point of the research we studied the conditions

(solution chemical composition, pH and potential regions) allowing a real copper passivation status, which could be useful in CMP processing. Pourbaix diagram (see Figure 1) indicates that copper passivity is expected in a pH range between 7 and 13. At pH values above 13, and at potentials above $-0.05 V_{SHE}$ copper is actively dissolved via the formation of soluble cuprite ions (CuO_2^{-2}). Furthermore, copper can be actively dissolved even in the pH range of 7-13 in the presence of chloride ions (Cl^-), glycine and ammonia (NH_3)¹. Thus, the goal of our studies was to find the conditions which can both provide copper passivity and are compatible with CMP processing requirements.

Our studies reported below lead to the following conclusion: The composition of copper CMP slurry should be consisted of ionic salt (MA) dissolved in aqueous media [in which M is alkaline metal cation (Li, Na, K, Sr) and A is the conjugated anion of a weak acid (for example hydroxide, acetate and carbonate ions)], with abrasive particles and oxidizers as well. This salts (MA) are actually bases, Lewis bases providing the basic pH range needed for passivation film to be developed. In order to achieve passivation potential the addition of oxidizers is required. The oxidizers can be organic (for example phenol compounds) or inorganic compounds (potassium iodate, potassium permanganate). The results reported below were obtain from sodium hydroxide based slurry, serving as an example for the application of dissolved ionic salt of the MA type.

We started our studies with 3 g/l sodium hydroxide solutions (NaOH, being the sodium salt of water) (pH = 12.5). At this pH value we expected copper passivity. The behavior of copper in sodium hydroxide solutions were extensively investigated by many authors in the last decade (17-25). Different analytical techniques, such as Raman spectroscopy (RS), electrochemical measurements, scanning tunneling microscopy (STM) and X-rays photoelectron spectroscopy (XPS), were used in these studies. The formation of different oxides including CuOH, Cu_2O , CuO (17-25) were recognized in these investigations. It should be noted that the formation of CuOH was observed by Maurice and co-workers (25) at the potential of $-0.675 V_{SHE}$. The formation of CuOH was confirmed by Marcus (26) with the use of STM studies, despite the fact that Cu oxides formation at potentials below $-0.2 V_{SHE}$ is not in agreement with Pourbaix diagram (Figure 1, this potential region is related to copper immunity in based

solutions). We studied the features of copper oxides formation in wide potential region from 1.5 V to 1 V in sodium hydroxide solutions.

3.1 Understanding Copper Electrochemistry in Hydroxide Solutions - Effect of Sodium Hydroxide Concentration.

In order to understand the effect of pH on copper oxidation in alkaline solutions we also evaluated solutions containing 0.3 and 30 g/l NaOH. The pH of these solutions were 10.5 and 14 respectively, while the pH of 3 g/l NaOH solution was 12.5. Pourbaix diagram (6) indicates that copper can be dissolved via the formation of soluble cuprite ions (CuO_2^{-2}) at pH's above 13.1. Thus, copper dissolution can be expected in 30 g/l NaOH in addition to copper oxidation.

The corrosion potential transient of copper measured during OCP exposure in sodium hydroxide solutions of 0.3, 3 and 30 g/l NaOH is shown in Figure 2. In aerated cell the corrosion potential sharply increases after immersion up to a certain value and practically remained constant during further exposure. The value of corrosion potential decreased with an increase in the sodium hydroxide concentration (Figure 4.2 a and b) in deaerated and aerated solutions. The values of corrosion potentials obtained after one hour exposure in aerated and deaerated cell are presented in Table I .

Table I . Copper corrosion potential values measured after one hour exposure in aerated and deaerated sodium hydroxide solutions.

	0.3 g/l	3 g/l	30 g/l
Aerated cell	-0.15 V	-0.21 V	-0.31 V
Deaerated cell	-0.375 V	-0.515 V	-0.56 V

The anodic potentiodynamic curves (scan rate of 5 mV/s) obtained from copper after one hour exposure in the alkaline solutions (0.3, 3 and 30 g/l NaOH, with and without deaeration) are shown in Figure 3. In aerated 30 g/l NaOH the onset of anodic current is detected at -0.32 V and a broad current peak (A_2) is observed in the anodic curve. With a decrease in NaOH concentration the onset of anodic current is shifted in the positive direction and the peak A_2 is markedly decreased. In 0.3 g/l the A_2 peak practically disappeared.

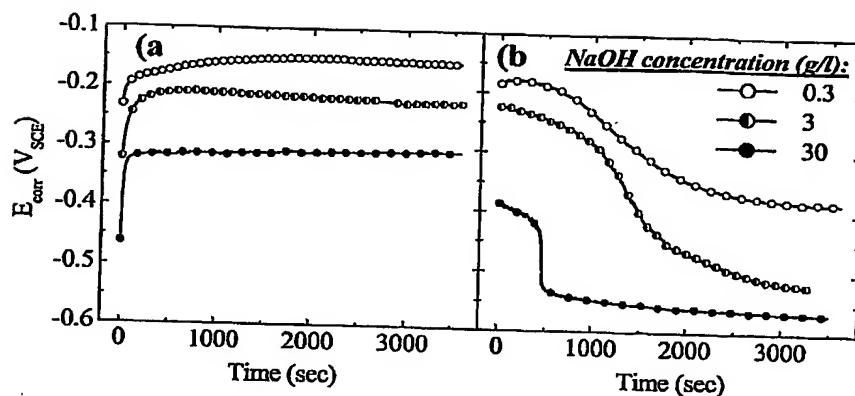


Figure 2. Corrosion potential transients of copper in different sodium hydroxide solutions; (a) aerated and (b) deaerated solutions at 25 °C.

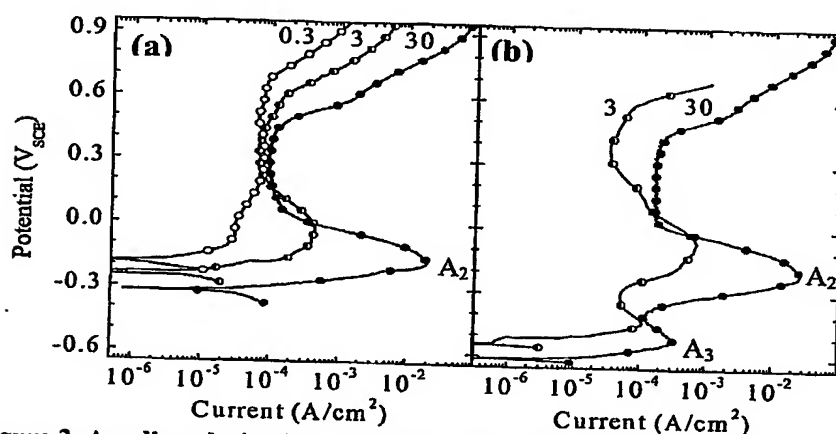


Figure 3. Anodic polarization curves obtained after one hour exposure to different sodium hydroxide solutions (a) without and (b) with deaeration at scan rate of 5mV/s (25 °C).

In deaerated solutions the onset of anodic current was observed at potentials below -0.5 V and an additional anodic peak, A₃, appeared at -0.5 V. In the solution of 3 g/l NaOH the anodic peak A₂ became smaller and shifted to more positive potential compared with 30 g/l NaOH solution.

Figure 4 presents the effect of cathodic pretreatment on the anodic behavior of copper electrode. These results were obtained at different scan rates (between 5 and 1000 mV/s). Subsequent to the cathodic pretreatment (-1.5 V for 5 min) the onset of

anodic current was observed to be at potentials below -1.0 V, in all the examined solutions. Additional anodic peaks (A_4 and A_5) were detected in the anodic profile obtained from all the solutions at a scan rates above 100 mV/s.

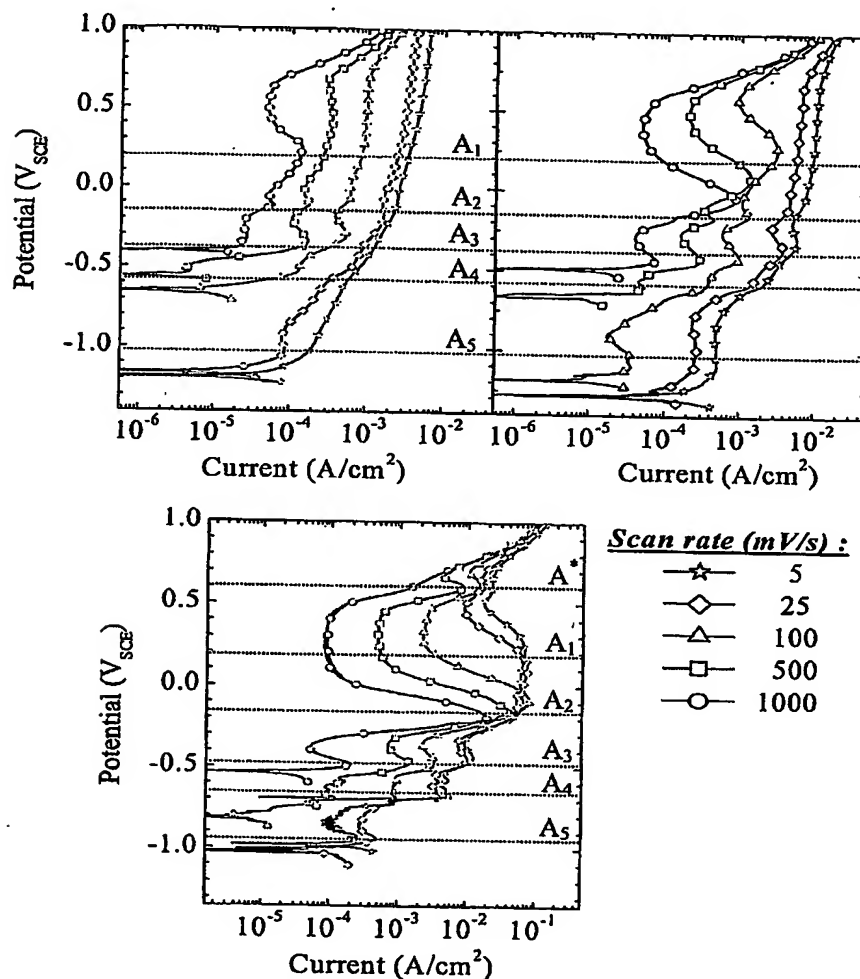


Figure 4. Anodic polarization curves of copper electrode measured at different scan rates subsequent to cathodic pre-treatment at -1.5 V for 5 min, at different concentrations of sodium hydroxide solutions: (a) 0.3 g/l, (b) 3 g/l, (c) 30 g/l.

The peaks sequence from A_1 to A_5 is clearly observed even in 0.3 g/l NaOH but the pronounced peaks were observed in 3 and 30 g/l solutions (especially in 30 g/l NaOH solution). For example, the anodic peak A_2 obtained at 5 mV/s is poorly detected

in 0.3 g/l NaOH compared with 3 and 30 g/l NaOH. The anodic currents obtained in all scan rates increased with increase in NaOH concentration.

We showed that increase in sodium hydroxide concentration causes a decrease in copper corrosion potential in solution with and without deaeration simultaneously. In highly concentrated sodium hydroxide solutions the anodic current peak A_2 is more pronounced (the peak is broader and detected at lower potentials). Similar copper electrochemical behavior was observed at polarization curves subsequent to cathodic pre-treatment at -1.5 V for 5 min, with different scan rates, at different sodium hydroxide concentrations.

3.2 Copper oxides Characteristics at potential region above -0.25 V.

The results obtained so far indicate that copper oxidation in sodium hydroxide solution strongly depend on the applied potential. From CMP application point of view the most important feature is the nature of copper oxidation at E_{corr} and in potential region above E_{corr} . This potential region can be achieved without external polarization or by the addition of an oxidizer. The corrosion potential of copper can be shifted from OCP to a positive direction in a wide potential range only by variation of oxidant additives and their concentration. This, by itself can provide strong variations in copper passivity.

In our work we studied copper passivity, morphology of copper oxides and copper oxides transformation in potential region above -0.4 V. A special attention was given to potential region above OCP (-0.25 V) in aerated solution. It should be noted that aerated solutions is more preferable for CMP processing (CMP application is inexpensive once there is no need for deaeration equipment).

At this stage of our study we examined the morphology of copper oxides formed at different potentials (A_1 , A_2 and A_3 peaks). These experiments were conducted with rounded copper coupons (0.5 cm radius and 2 mm thick, 99.9995% purity) polished with a 1 μ m diamond paste. The oxide growth was conducted using potentiostatic exposure for 30 min at the examined potentials (-0.4 V (A_3), -0.15 V (A_2), and 0.3 V (A_1)), this potential was applied only after cathodic pre-treatment for 5 minutes at -1.5 V. Subsequent to potentiostatic exposure, the specimens were rinsed with DI water, dried and examined by HRSEM.

The current transient measured during the exposure of the copper electrode at different applied potentials is shown in Figure 5. Following the application of -0.4 V, the anodic current rapidly decreased down to a value lower than $1 \cdot 10^{-5}$ A/cm², pointing on the formation of copper oxide layer covering the surface. At -0.15 V the anodic current transient was observed to be completely different at the first 20 seconds. Once the potential was applied the anodic current rapidly decreased down to $1 \cdot 10^{-4}$ A/cm² as was previously observed. However, during further exposure (200 sec) a peak in the profile of the anodic current transient with a maximum value of $8 \cdot 10^{-4}$ A/cm² is observed. After 600 sec the anodic current decreased down to $1 \cdot 10^{-5}$ A/cm². The anodic current peak observed during copper exposure at -0.15 V is attributed to alteration in the nature of copper oxide. The anodic current at 0.1 V is gradually decreased during exposure as was observed at -0.4 V. However, unlike the situation observed at -0.4 V the decrease in the anodic current at 0.1 V was much slower, especially during the first 200 sec. No peak of anodic current was detected during exposure at 0.1 V. The detected peak was very small and observed after 10 sec exposure. During further exposure the anodic current decreased to very low values ($\sim 1 \cdot 10^{-5}$ A/cm² after 200 sec exposure). The different anodic current transient profiles measured at different applied potentials are associated with variations in the oxide films nature.

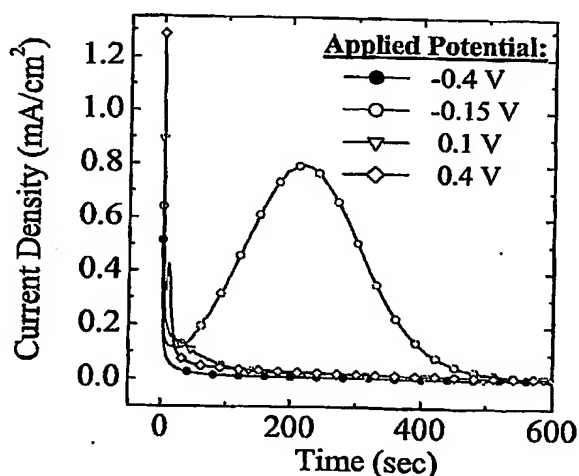


Figure 5. Current transient of copper measured with potentiostatic exposure of copper electrode at different applied potentials in 3 g/l NaOH solution.

Figure 6 presents different fragments of surface morphology of polished (as-received) and exposed copper surface exposed to different applied potentials corresponding to the anodic peaks A₁, A₂ and A₃ in 3 g/l sodium hydroxide solution. Figures 6b and 6c present the surface morphology developed on copper after 30 min exposure at -0.4 V. The copper oxide (apparently Cu₂O) covering the electrode surface after exposure at -0.4 V is characterized as a dense layer with a deposition of small globular crystals. The average dimensions of these crystals were measured to be 50-100 nm. The morphology of the copper surface after exposure at -0.15 V was completely different (see Figures 6d and 6e). The whole surface was covered with a thick crystalline layer (probably CuO). This deposit had two-layer structure: the first layer consisted of small elongated crystals (far below 1µm) while the upper layer was constructed of large crystals exhibiting needle like shape. No deposits were observed after exposure to 0.3 V (even at magnification of ×200,000, Figures 6f and 6g). The copper surface after exposure to 0.3 V has not changed and was similar to a freshly polished surface. One can suggest that the copper oxide that formed at 0.3 V was very thin and dense.

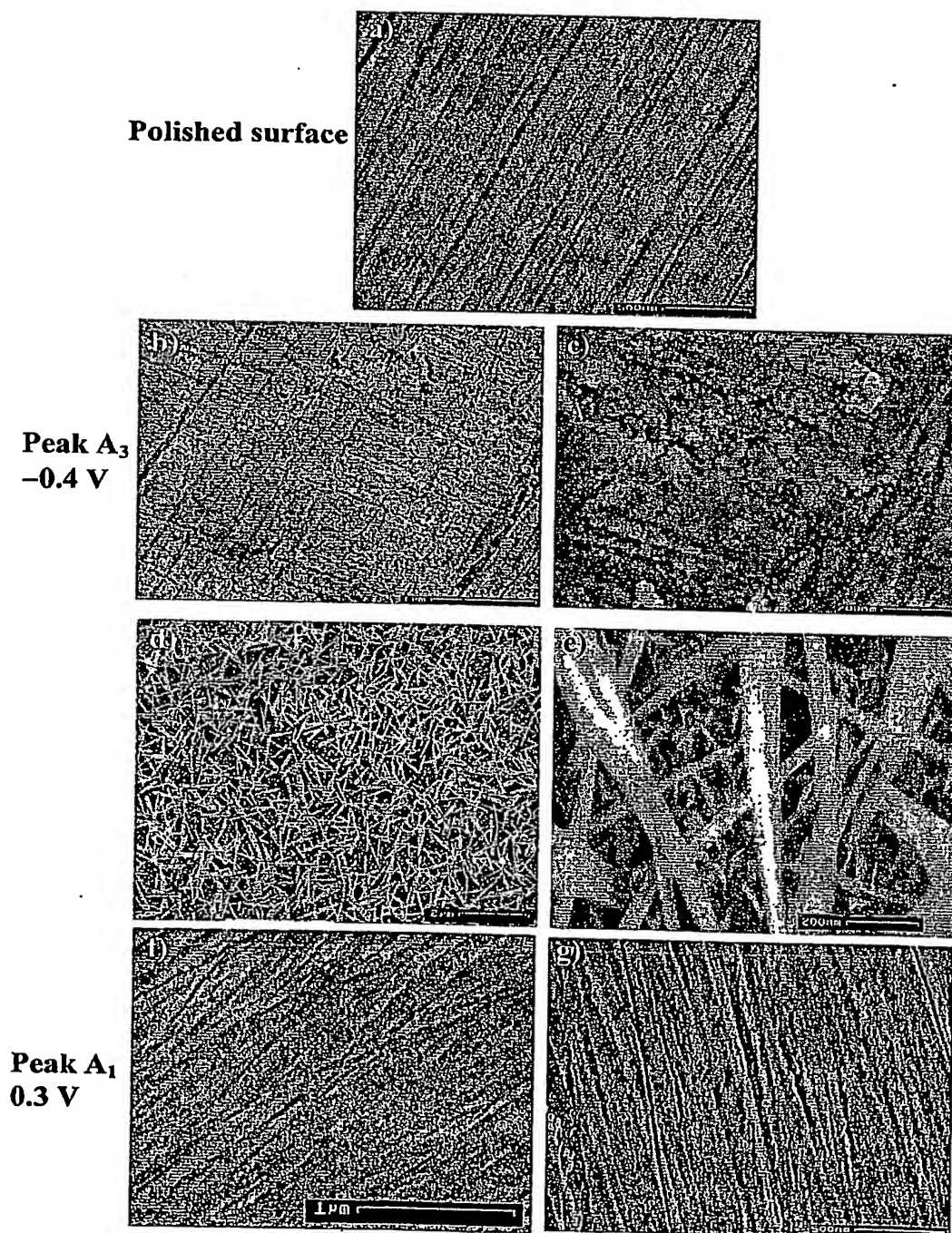


Figure 6. Different fragments of copper surface after 30 minutes exposure at different applied potentials in 3 g/l NaOH solution: (a) polished surface, (b) and (c) -0.4 V, (d) and (e) -0.15 V, (f) and (g) 0.3 V.

In order to determine the variations in copper oxides coating formed during copper exposure at OCP, the morphology of copper surface developed at different stages of OCP exposure was compared to the morphology obtained at different applied potentials. The results are shown in Figure 7. Figure 7a was obtained after 30 min exposure at OCP in 3 g/l NaOH solution. Only traces of copper oxide were detected on the copper surface at this stage. The surface morphology obtained after 30 min exposure at OCP was very similar to the one detected at -0.4V (Figure 6b). After one hour exposure, the copper surface was covered with a deposits of both short ($\sim 100\text{ nm}$) and long ($\sim 2\text{ }\mu\text{m}$) needle shaped crystals. During further exposure the changes observed were related only to the sizes of crystals. After 2.5 hours the size of both short and long crystals increased up to 250 nm and $\sim 5\text{--}7\text{ }\mu\text{m}$, respectively. After 5 hours exposure the short crystals reached $\sim 500\text{ nm}$ length. Contrary to these small crystals the long ones were distorted. It should be noted that the morphology of copper electrode obtained during OCP exposure differs from the detected morphology at -0.15V (see Figure 6d and 6e).

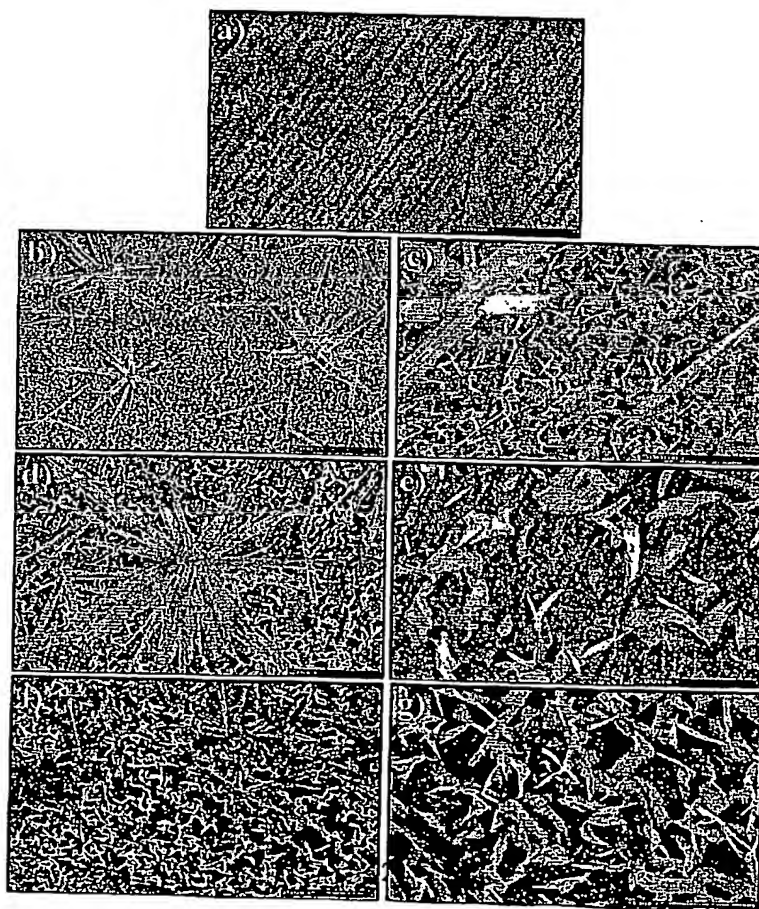


Figure 7. HRSEM micrographs of copper surface subsequent to different time exposure to OCP in 3 g/l NaOH solution: (a) 30 min; (b) and (c) 60 min; (d) and (e) 160 min; (f) and (g) 300 min.

Based on these results we can conclude that the copper surface exposed at potentials below 0.0 V is covered with flaky deposits of oxides. At potential above 0.0 V copper surface is covered with very thin, dense film of oxides. The formation of copper oxides at different potentials and the transformation from one oxide species to another one is of great interest in this patent discloser.

3.3 Determination of Copper Passivation Potential Range Needed for CMP Process

The transformation of Cu-oxides was studied using the method of corrosion potential decay. We used the following procedure: copper electrode was first exposed to -0.15 V for 10 minutes and after that to more positive potential. In some cases the copper electrode was directly exposed to potential above 0.0V. After interruption of potentiostatic exposure we have measured the corrosion potential decay. The obtained results are shown in Figures 8 and 9. Figure 8 presents results of corrosion potential decay obtained after 10 minutes exposure to -0.15 V followed with a shift in the applied potential to more positive values and further exposure for 30 min at the new applied potential.

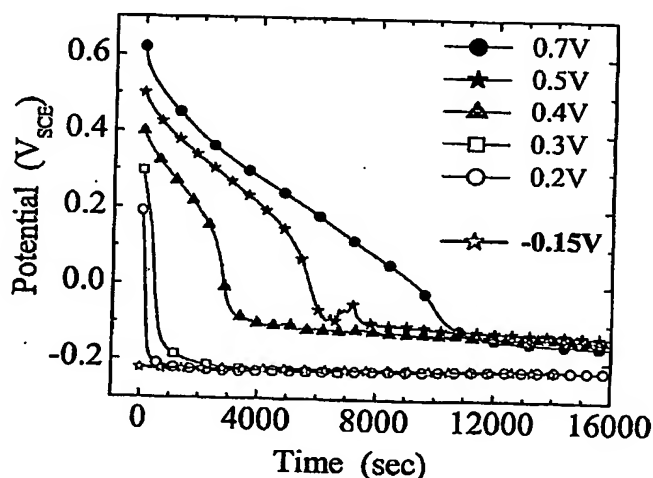


Figure 8. Corrosion potential transient of copper electrode obtained in 3 g/l sodium hydroxide solution subsequent to different pre-treatments: 10 minutes exposure to -0.15 V followed by 30 min exposure to more positive potentials.

We can see that interruption of electrode exposure at -0.15 V is accompanied with rapid decrease in the corrosion potential down to values slightly below -0.2 V. Similar results were also obtained once exposure to -0.15 V was followed with further exposure to 0.2 and 0.3 V. As can be seen, the interruption of polarization at 0.2 and 0.3 V is also accompanied with rapid drop to the values below -0.2 V. The situation changed if pre-exposure at -0.15 V was followed by the potentiostatic exposure at 0.4 V and higher potentials. As can be seen the marked potential delay occurred in the decay curves obtained after exposure to potentials higher than 0.3 V. The higher was the potential applied after exposure to -0.15 V the longer was the potential delay in the decay curves. It is reasonable to assume that exposure at potentials 0.2 and 0.3 V after pre-treatment at -0.15 V is accompanied with the formation of very thin oxides on the electrode surface. At potentials above 0.3 V either the thickness (or amount) of new phase increased or the transformation of oxides formed at -0.15 V into a new one occurred.

In order to determine the role of copper oxides covering electrode surface after exposure to -0.15 V and the nature of copper oxides formed at potentials above 0.0 V we have examined the potential decay after exposure at 0.7 V with and without pre-treatment at -0.15 V. The obtained results are shown in Figure 4.2-20. As can be seen once the potential of 0.7 V was applied without pre-treatment at -0.15 V the corrosion potential rapidly decreased without intermediate delay. Unlike that, the exposure at 0.7 V after pre-exposure at -0.15 V results in a significant potential delay. The longer was the exposure of the pre-treated electrodes at 0.7 V the wider was the potential delay. It should be also noted that in all the cases when the delay occurred, the corrosion potential during long term exposure reached the potential values of approximately -0.15 V. These results serve as an evidence that the nature of copper oxides formed at potential above 0.0 V strongly depends on the initial surface state of copper (or copper pre-treatment). It can be suggested that two different copper oxides are formed on the

copper surface at potentials above 0.0 V. The thin oxide film is covering the electrode surface in the case of bare copper. If the copper oxide was formed on electrode surface during exposure at potentials below 0.0 V, the transformation of initial copper oxide to new one takes place by shifting the applied potential to 0.7 V.

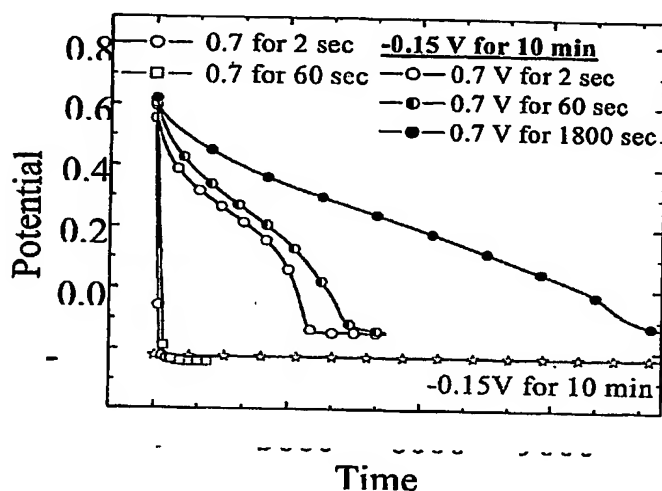


Figure 9. Corrosion potential transient of copper electrode obtained in 3 g/l sodium hydroxide after different potentiostatic pre-treatments.

Thus, we can conclude that the potential region between 0.0 V and 0.7 V is characterized by the formation of two different copper oxides. The electrochemical measurements conducted in this work indicate that these oxides are different from the oxides formed at potentials below 0.0 V. The copper oxides formed at potentials below 0.0 V undergo transformation during increase of applied potentials above 0.0 V.

The difference between copper oxide morphologies developed during potentiostatic exposure at -0.15 V and 0.7 V is clearly seen in Figures 10a and 10b. Figure 10 shows the transformation of copper oxide formed at -0.15 V after an increase in the applied potential to 0.7 V and further exposure for 30 min. As can be seen, copper oxide formed on the untreated copper surface at 0.7 V is dramatically different from the morphology observed at -0.15 V. The oxide formed is thin and dense

(see Figure 10b). Figure 10c presents the morphology developed at the copper surface exposed at 0.7 V for 30 min after a pre-treatment process at -0.15 V for 10 minutes. At -0.15 V, copper oxide has two layer structure; small crystals in the first layer and large crystals on the upper layer. Comparing Figures 10a and 10c indicates that by applying a potential of 0.7 V the first layer disappeared.

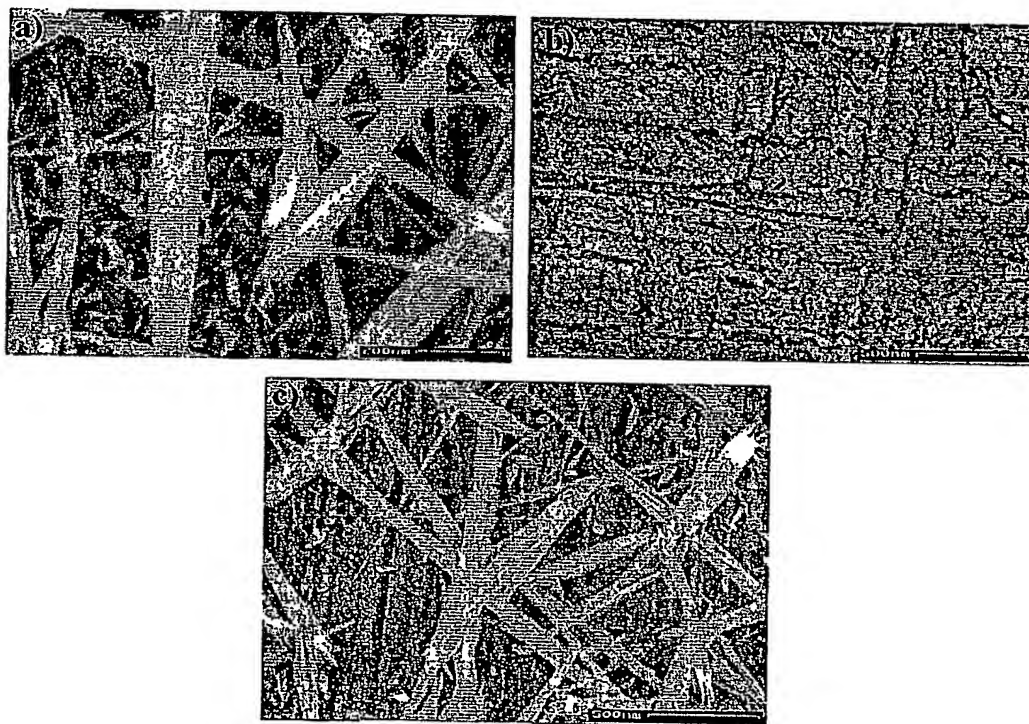


Figure 10. Fragments of copper surface developed in 3 g/l NaOH at different potentials: (a) -0.15 V for 10 minutes, (b) 0.7 V for 15 minutes, (c) initially pre-treated at -0.15 V for 10 minutes followed by 0.7 V potential for 60 sec.

4. Conclusions

We can summarize that copper oxides formed in sodium hydroxide solution at potentials above 0.0 V and in the pH range of 7-12 are the most applicable for copper CMP application. These oxides are highly dense, thin and behave as a passive film.

The combination between basic solution and oxidizer, replacing the potential power supply, providing a passivation potential up to 0.7V (potentials of 0.3-0.4V will be sufficient), can produce a novel slurry chemistry developed for copper CMP applications.

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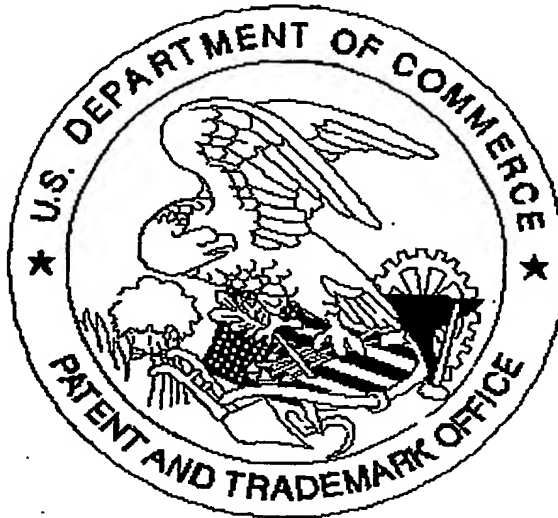
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Claims:

1. A Copper CMP slurry composition, essentially as described and exemplified herein.
2. Copper CMP slurry composition comprising at least one ionic salt (MA) in which M is alkaline metal cation (Li, Na, K or Sr) and A is the conjugated anion of a weak acid, such as hydroxide, acetate and carbonate and at least one oxidizer, such as an organic oxidizer (e.g., phenol compounds) or inorganic oxidizer.

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